Preparation and characterization of magnesium ion gel polymer electrolytes for application in electrical double layer capacitors

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ABSTRACT

This work describes the preparation and characterization of poly (methyl methacrylate) (PMMA) based gel polymer electrolytes with magnesium triflate (Mg(CF3SO3)2) as the ion providing salt. Liquid electrolytes containing 0.4 M Mg(CF3SO3)2 in solvents comprising different ratios of ethylene carbonate (EC) and diethyl carbonate (DEC) have been prepared at room temperature. The highest conducting electrolyte contains EC and DEC in the weight ratio of 2:1. To the highest conducting liquid electrolyte, 25–50 wt.% PMMA has been added and the mixtures were heated at 80 °C for 2 min to form gel polymer electrolytes. The gel electrolyte with composition 40 wt.% PMMA and 60 wt.% of 0.4 M Mg(CF3SO3)2 in EC:DEC (2:1, w/w) has the highest conductivity of 5.58 × 10−3 S cm−1 and activation energy 0.11 eV. The gel polymer electrolyte with highest conductivity at room temperature has Mg2+ ion transference number of 0.37 and electrochemical stability window 2.42 V. The highest conducting gel polymer electrolyte has been used to fabricate an electric double layer capacitor (EDLC) which exhibits a nearly rectangular voltammogram even after the 50th discharge cycle. The capacitance of the EDLC is about 27 F g−1 after the 1st cycle and 23 F g−1 after the 50th cycles.

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1. Introduction

The development of polymer electrolytes has drawn the attention of researchers from all over the globe. This is due to the many potential applications of polymer electrolytes in electrochemical devices such as lithium ion batteries, electrochromic devices and electric double layer capacitor (EDLC). Ion conducting polymer electrolytes have many advantages compared to liquid electrolytes. These advantages include being leak proof and non-bulky [1]. For applications in an all solid-state electrochemical device, ion conducting polymer electrolytes should possess sufficient electrical conductivity, good mechanical strength and thermal stability and have appreciable cationic transference number [2–5]. They should also be compatible with the electrodes used. To date, three classes of polymer electrolytes have been established. They are dry solid-state, gel plasticized and composite polymer electrolytes. Gel polymer electrolytes (GPEs) can be produced when the polymer swells up in an organic solvent. GPEs can provide better contact with the electrode surface compared to dry solid electrolytes [6,7]. Low molecular weight organic solvents such as dimethyl sulfoxide (DMSO), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC) and propylene carbonate (PC) can be used to improve the electrolyte conductivity. The last two solvents are the most frequently used to prepare gel polymer electrolytes due to their high dielectric constant and low viscosity, respectively [8–10]. Although many gel polymer electrolytes have been reported, most research focus on Li+ ion conducting electrolytes [11–13]. The ionic radius of Li+ and Mg2+ is about the same, i.e. 68 and 65 pm, respectively; hence it is possible to replace Li+ ions with Mg2+ ions as the charge carrier in gel polymer electrolytes.Magnesium metal is more stable compared to lithium metal. It is easier to handle magnesium metal in oxygen or humid atmosphere compared to lithium metal. To handle lithium metal argon or helium atmosphere is required. Magnesium metal is more abundant in nature compared to that of lithium and magnesium metal is much cheaper than lithium. Studies on polymer electrolytes using Mg2+ ions as the charge carriers are being intensively undertaken [14–19].

In this work, gel polymer electrolytes were prepared by adding poly (methyl methacrylate) (PMMA) to liquid electrolytes comprising magnesium triflate Mg(CF3SO3)2 in binary solvent mixtures containing different ratios of ethylene carbonate (EC) and diethyl carbonate (DEC). The GPEs were then characterized using Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (EIS). The electrolyte decomposition voltage was determined using linear sweep voltammetry (LSV). The highest conducting magnesium ion gel polymer electrolyte was employed in EDLC fabrication. Cyclic voltammetry (CV) was performed in the voltage range between 0 and 0.85 V at a constant current of 1 mA
to investigate the capacitive behavior of the EDLC. The EDLC was cycled in order to determine the capacitance.

2. Experimental

2.1. Materials

Poly (methyl methacrylate) (PMMA; MW: ~996,000), magnesium trifluoromethane-sulfonate or magnesium triflate, [Mg(CF₃SO₃)₂ or MgTr], ethylene carbonate (EC) and diethyl carbonate (DEC) were purchased from Sigma–Aldrich and used as received without further purification.

2.2. Preparations of gel polymer electrolytes

A solution cast method was used to produce gel polymer electrolyte (GPE) films. First, the liquid electrolytes were prepared by dissolving magnesium triflate in solvents consisting different weight ratios of EC and DEC to form a liquid electrolyte of concentration 0.4 M MgTr. The ratio of the solvents (EC:DEC) that exhibited the highest conductivity was used to prepare GPE. The highest conducting liquid electrolyte was then mixed with different amounts of PMMA (25–50 wt.%) and stirred magnetically for 2 h. The viscous mixtures were cast into different glass petri dishes and were heated at 80 °C for 2 min. Finally, free standing GPEs (thickness ~400–450 μm) was formed upon cooling at room temperature. The method of preparation followed Kumar et al. [16,17].

2.3. Preparations of electrodes

The electrodes for EDLC were prepared by mixing 80 wt.% activated carbon (BP20) purchased from SANWA Components Inc., USA, 10 wt.% of carbon black (Super P) and 10 wt.% of poly(vinylidene fluoride) (PVDF) in N-methylpyrrolidone. The mixture was stirred until a homogeneous slurry was obtained. An aluminum mesh was washed with ethanol and the slurry was spread on the mesh using the doctor blade method. The aluminum mesh with coated electrode was heated at 60 °C in a vacuum oven for 30 min and the electrode was pressed at 250 mbar to ensure good contact between electrode and aluminum mesh.

2.4. Characterization

The thermal stability of GPEs was measured using TA Instruments (Q200) differential scanning calorimetry (DSC). The samples were placed in sealed aluminum pans and heated at 20 °C min⁻¹ from room temperature to 105 °C and maintained for 4 min to remove traces of water and solvent. The samples were then rapidly cooled to 30 °C and then reheated to 400 °C at a heating rate of 10 °C min⁻¹. The final heating scan was used to evaluate the glass transition (Tg) and decomposition (Td) temperatures. FTIR spectra were taken with the Thermo Scientific Nicolet iS10 Smart ITR spectrometer in the wavenumber region from 650 to 4000 cm⁻¹ and resolution 1 cm⁻¹.

Fig. 1 shows the cell used to measure the conductivity of liquid electrolyte with stainless steel plates as electrodes. Conductivity of liquid electrolyte, σ, can be calculated from the equation σ = τ/(R0A) where τ is distance between electrodes, A is the contact area between stainless steel electrode and the electrolyte, and R0 is the bulk resistance obtained from the Cole–Cole plot. Impedance measurement was carried out using the computer-interfaced Hioki LCR 3531 bridge computer in the frequency range from 50 Hz to 1 MHz. For GPE, the impedance of the prepared gel was measured using the same instrument in the temperature range from 25 to 80 °C. The gel electrolyte films were sandwiched between two stainless steel electrodes. The conductivity, σ, was calculated using the above mentioned equation.

DC polarization method was used to measure the transport number of the GPE. The DC current is monitored as a function of time on application of a fixed 0.7 V DC voltage across the sample. In this study, stainless steel and magnesium metal were used as blocking and non-blocking electrode, respectively. The transferance number was calculated from the polarization current versus time plot using the equation ñMg = I Mg − I s / I Mg where I Mg and I s are the initial and final steady state currents.

The electrochemical stability window of the gel electrolyte was studied by linear sweep voltammetry (LSV) using the Auto-lab PGSTAT12 potentiostat–galvanostat. The voltage range studied was from −4 to 5 V. LSV was performed using a three-electrode configuration; stainless steel (SS) as the working electrode and a magnesium metal as both the reference and counter electrodes. The GPE was used as separator between stainless steel and magnesium metal. Sample preparation was carried out in the glove box.

Cyclic voltammetry and galvanostatic charge–discharge cycling of EDLC were performed using CH Instrument model 600D series and Neware battery cycler, respectively. Cyclic voltammetry tests were conducted at scan rate 5 mV s⁻¹ between 0 and 0.85 V in a two-electrode configuration. Galvanostatic charging–discharging test was performed in the voltage range between 0 and 0.85 V at a constant current of 1 mA.

3. Results and discussion

Liquid electrolytes were prepared by dissolving MgTr to supply Mg²⁺ ions in the binary solvent mixtures of EC:DEC. EC is chosen since it has high dielectric constant (ε = 89) which is advantageous for the dissolution of a salt. EC is present in powder form at room temperature and therefore a co-solvent is required to dissolve it. The co-solvent chosen in this work is DEC which at room temperature is in liquid form. Its room temperature viscosity is low, η = 0.74 cP. Thus a binary mixture where one component has high dielectric constant and the other low viscosity would make a good solvent combination. In order to get the appropriate EC:DEC ratio that would give the highest room temperature conductivity on incorporation of MgTr, five different ratios of EC:DEC binary solvents were prepared. The five ratios were EC:DEC = 2:1, 2:3, 1:1, 1:2 and 3:2. Table 1 lists the calculated dielectric constant value of the solvents following the method of Singh et al. [20] and the conductivity of the 0.4 M MgTr liquid electrolytes in different weight ratios of EC and DEC.

From Table 1, the highest conducting liquid electrolyte is 0.4 M Mg(CF₃SO₃)₂ in EC and DEC with weight ratio EC:DEC = 2:1. The conductivity is 1.88 × 10⁻³ S cm⁻¹. This conductivity value is about
the same order of magnitude with that reported by Singh et al. [20] for 0.4 M LiCF3SO3 dissolved in a binary solvent of DMA:DEC of the same ratio. Pandey et al. [21] obtained a conductivity of 4.8 × 10−3 S cm−1 for 0.3 M MgTr in EMIT and 3.4 × 10−3 S cm−1 for 0.3 M MgTr in EMIT/PVDF-HFP (w/w = 4/1) at room temperature.

The gel polymer electrolyte consists of high conducting liquid electrolyte entrapped in a polymer matrix. Fig. 2 shows the variation of conductivity with the PMMA content from 25 to 50 wt.%. Gels are not easily formed at lower concentrations of PMMA. At PMMA concentrations from 25 to 40 wt.%, the conductivity of the GPEs increased from 4.54 × 10−5 S cm−1 to 5.58 × 10−5 S cm−1 and at PMMA concentrations above 40 wt.%, the conductivity decreased and dropped to 3.51 × 10−5 S cm−1 at 50 wt.% PMMA content. The variation in conductivity with PMMA content may be attributed to the amor phousness of the samples.

Fig. 3 depicts the DSC thermograms for gel electrolytes containing 35, 40 and 45 wt.% PMMA. The endothermic peak at 369°C corresponds to the decomposition temperature of PMMA. When dissolved in EC/DEC mixed solvents and liquid electrolyte EC/DEC/MgTr, the decomposition temperature increased to 370 and 371°C, respectively. The enthalpy of decomposition for the gel sample containing 45 wt.% PMMA is −291 J g−1. If this sample is taken as reference (i.e. having 100% degree of crystallinity) and since the conductivity of this sample is lower than the gels containing 40 and 35 wt.% PMMA, the degree of crystallinity of the 40 and 35 wt.% PMMA containing gels can be obtained by dividing its enthalpy of decomposition with 291 J g−1. Thus the degree of crystallinity of the 40 wt.% PMMA containing sample is ∼42%. The degree of crystallinity for the 35 wt.% PMMA containing gel is therefore ∼84% since its conductivity is higher than the gel electrolyte containing 45 wt.% PMMA. Hence, the variation in conductivity can be attributed to the amorphousness of the samples.

The presence of free ions, ion aggregates and undissociated salt in gel polymer electrolyte have also been studied by FTIR spectroscopy to explain the variation of conductivity with PMMA content. According to Jeong et al. [22], clear distinctions between free ions, contact ion pairs and higher ion aggregates can be observed from the triflate anion band. Ion association occurs at the SO3 end of the anion. Therefore, the symmetric SO3 stretching mode is highly sensitive to changes in the coordination state of the anion. Upon decomposition of the SO3 band, free triflate ions should peak at 1032 cm−1. Bands due to ion pairs and large ion aggregates should peak at 1051 and 1062 cm−1, respectively [23–25]. Fig. 4(a)–(f) depict symmetric SO3 stretching mode for PMMA–MgTr in EC/DEC (2:1) with (a) 25, (b) 30, (c) 35, (d) 40, (e) 45 and (f) 50 wt.% PMMA concentrations. A band that peaks at 1030 cm−1 attributed to free ions is observed in all spectra. In the wavenumber region from 1040 to 1100 cm−1, three decomposed bands that peak at approximately 1060, 1070, 1080 cm−1 are observed. Large ion aggregates are represented by the band that peaks at 1060 cm−1. The bands that peak at 1070 and 1080 cm−1 are ring breathing and skeletal stretching of the carbonate solvents. The area of each band is representative of abundance of the above mentioned entities. Fig. 5 shows the area of each band with respect to the PMMA concentration. It is to be noted that in this work, the amount of salt is fixed. Even at 25 wt.% PMMA concentration, there exist ion aggregates which do not contribute to conductivity. The amount of free ions and non-conducting ion aggregates are quite constant until 40 wt.% PMMA has been added where the free ions curve exhibit a maximum. The non-conducting ion aggregates curve exhibits a minimum at 40 wt.% PMMA concentration. PMMA has a dielectric constant of ∼2.6 [26]. As the PMMA concentration increases from 25 to 40 wt.%, the polymer also contributes in dissociating the non-conducting large ion aggregates into mobile ions. Ion dissociation to give free ions and ion association to form neutral ion pairs are equally competitive at 25 and 30 wt.% PMMA content. From Fig. 5, a significant increase in ion dissociation is observed from 35 wt.% PMMA content. Above 40 wt.% PMMA content ion association becomes significant compared to dissociation. Moreover, viscosity increases with PMMA content. From the results

| Table 1 Conductivity of 0.4 M MgTr liquid electrolyte in different ratios of EC and DEC solvent at 25 °C. |
|-----------------|-------------------|------------------|
| EC/DEC (w/w)    | Calculated dielectric constant, ε | σ (S cm⁻¹ × 10⁻²) |
| 2:1             | 60.40              | 1.88             |
| 2:3             | 37.52              | 1.08             |
| 1:1             | 46.10              | 1.54             |
| 3:2             | 54.68              | 1.01             |
| 1:2             | 31.80              | 1.84             |
depicted in Fig. 5, it can be understood why the conductivity-PMMA concentration plot (Fig. 2) exhibits a maximum at 40 wt.% PMMA content. On addition of 45 and 50 wt.% PMMA to the highest conducting liquid electrolyte, the drop in conductivity can be explained by the decrease in free ions concentration and the increase in large ion aggregates as depicted in Fig. 5. Above 40 wt.% PMMA concentration, ionic mobility decreases due to increase in viscosity of the GPEs. The attractive coulombic forces become sufficiently effective that large ion non-conducting aggregates are again formed. It can be observed in Fig. 5 that at 50 wt.% PMMA concentration the free ion and large ion aggregates concentration are about equal. According to Kumar et al. [27], the presence of a maximum in the plot of Fig. 2 suggests the occurrence of two competing processes. High free ion concentration implies more ion dissociation over ion reassociation and vice versa. Viscosity can also affect ionic mobility. The high viscosity attributed to the high PMMA content reduces ionic mobility leading to the drop in conductivity [28,29].

The plot of conductivity for the highest conducting GPE film as a function of reciprocal temperature is shown in Fig. 6. The temperature range is from 30 °C to 80 °C. The plot showed that conductivity of the GPE increased from $5.58 \times 10^{-5}$ S cm$^{-1}$ at 303 K to $1.66 \times 10^{-4}$ S cm$^{-1}$ at 353 K. The regression value, $R^2$ for the plot of log$\sigma$ versus 1000/$T$ is almost unity suggesting that the plot can be considered linear thus obeying the Arrhenius equation,

$$\sigma = A_0 \exp(-E_a/kT)$$

where $E_a$ is activation energy, $k$ is Boltzman constant and $A_0$ is pre-exponential factor. Using the value of the slope and Arrhenius equation, $E_a$ value for all samples calculated is in the range between 0.11 and 0.17 eV. The variation of $E_a$ with PMMA content is tabulated in Table 2. The activation energy value obtained in the work is within the range between 0.03 and 0.36 eV as reported by Kumar et al. [16] for PMMA–MgTr–EC–PC. Difference

**Fig. 4.** Symmetric SO$_3$ stretching mode for gel electrolytes containing (a) 25, (b) 30, (c) 35, (d) 40, (e) 45 and (f) 50 wt.% PMMA in the region (I) free triflate ions; (II) large ion aggregates; (III) EC skeletal stretching; (IV) EC ring breathing.

**Fig. 5.** The plot of area under assigned decomposed free ion band (—) and large ion aggregate band (—) versus the concentration of PMMA.
in the activation energy value may be due to the dielectric constant 
of the solvents used to dissolve PMMA and MgTr. Kumar et al. [16] 
used PC and EC as the solvents and these have high dielectric 
constants being 64.92 and 89, respectively. In this work, EC and 
DEC were used as solvents to dissolve PMMA and MgTr. The dielectric 
constant of DEC is 2.81. The higher dielectric constant of PC 
compared to DEC enables higher rate of ion dissociation. Since the log $\sigma$ 
versus $10^3/T$ plot is Arrhenian, it may be inferred that the Mg$^{2+}$ ion 
is transported via hopping mechanism.

Fig. 7(a)–(c) shows the polarization current graph as a function 
of time for 25, 40 and 45 wt.% PMMA added to 0.4 M MgTr in EC:DEC 
(2:1) solvents. The calculated transport numbers of Mg$^{2+}$ are tabulated 
in Table 2. The transport number of Mg$^{2+}$ containing 40 wt.% 
of PMMA is higher compared to that of 25 wt.% and 45 wt.% PMMA 
containing gel electrolyte. Kumar et al. [16] reported the Mg$^{2+}$ ion 
transport number of 0.33 at room temperature for PMMA-based 
electrolyte containing MgTr. In our work, the value of ion transport 
number of Mg$^{2+}$ is 0.37 for the highest conducting gel polymer 
electrolyte containing 40 wt.% PMMA.

The electrochemical stability of the gel polymer electrolyte 
was obtained by linear sweep voltammetry (LSV). From Fig. 8, 
the cathodic and anodic decomposition occurred at nearly 2.42 V 
for the highest conducting GPE which contains 40 wt.% of 
PMMA and 60 wt.% of 0.4 M MgTr in EC:DEC (2:1). Oh et al. 
[30] reported a decomposition voltage at 4.3 V using P(Vdf-co-HFP)–Mg(ClO$_4$)$_2$–EC/PC. A high electrochemical stability may be 
due to the (a) dielectric constant, $\varepsilon_r$ of the polymer and (b) lattice 
energy of the salt. The dielectric constant of PMMA is 2.6 [26] and 
for P(Vdf-co-HFP) is 8.4 [31]. A high dielectric constant of the polymer 
will give a higher concentration of charge carriers. The lattice 
energy of MgTr and Mg(ClO$_4$)$_2$ is 2039 kJ mol$^{-1}$ and 2005 kJ mol$^{-1}$, 
respectively.

The cyclic voltammetry (CV) of the EDLC was also studied at 
5 mV s$^{-1}$ scan rate in the voltage range between 0 and 0.85 V as 
shown in Fig. 9 for 1st and 50th cycles of charge and discharge. The 
EDLC shows near to rectangular shape voltammogram even up to 
50th cycle and there are no visible peaks due to redox reactions. The 
50th cycle voltammogram deviates from the rectangular shape due 
to ohmic drop [32].

Fig. 10 shows the typical charge–discharge characteristics 
of EDLC employing the highest conducting gel electrolyte containing 
40 wt.% PMMA. The cut-off voltage EDLC was charged up to 
0.85 V. The discharge characteristics (Fig. 11) have been found to be 
almost linear, which confirms the capacitive behavior of the EDLC 
cell. The discharge capacitance for the first cycle of the EDLC is calculated 
from the slope to be 27 F g$^{-1}$. Pandey et al. [21] reported a 

<table>
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<th>PMMA content (wt.%</th>
<th>$\sigma$/Sm$^{-1}$</th>
<th>$E_a$/eV</th>
<th>$t_r$</th>
</tr>
</thead>
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<tr>
<td>25</td>
<td>4.54 × 10$^{-5}$</td>
<td>0.14</td>
<td>0.10</td>
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<tr>
<td>30</td>
<td>4.64 × 10$^{-5}$</td>
<td>0.13</td>
<td>–</td>
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<tr>
<td>35</td>
<td>4.95 × 10$^{-5}$</td>
<td>0.12</td>
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<tr>
<td>40</td>
<td>5.58 × 10$^{-5}$</td>
<td>0.11</td>
<td>0.37</td>
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<tr>
<td>45</td>
<td>3.82 × 10$^{-5}$</td>
<td>0.16</td>
<td>0.09</td>
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<tr>
<td>50</td>
<td>3.51 × 10$^{-5}$</td>
<td>0.17</td>
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Fig. 8. Linear sweep voltammetry of Mg/GPE/SS at scan rate 5 mV s$^{-1}$.
capacitance between 64 and 82 mF cm\(^{-2}\) using the electrolyte consisting of poly(vinylidene fluoride–hexafluoropropylene) in EC:PC and doped with MgTr salt. Hashmi et al. [33] have studied performance of EDLC using PMMA dissolved in EC:PC with LiClO\(_4\) and NaClO\(_4\) doping salts. The capacitance obtained is 16 and 19 F g\(^{-1}\), respectively.

4. Conclusions

Liquid electrolyte solution of MgTr salt in a binary solvent EC/DEC has been immobilized in PMMA polymer host to form a magnesium ion gel polymer electrolyte. The highest conducting GPE \(5.58 \times 10^{-3}\) S cm\(^{-1}\) is obtained with a composition of 40 wt.% PMMA and 60 wt.% of 0.4 M MgTr in EC:DEC (2:1). FTIR studies showed the increased conductivity is due to the increase of free ions and decrease in non-conducting large ion aggregates. The capacitance of EDLC employed magnesium ion based gel polymer electrolyte is 23 F g\(^{-1}\) after the 50th cycle.

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References